



Study of the Physicochemical Properties of Recycled PVX

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ABSTRACT

Recycling waste PVX compared to polyolefins is a bit difficult, so the products made from them have a complex chemical composition, that is, various additives will be added. Given these problems, it is possible to obtain various types of secondary products, modifying them by adding special components that facilitate the processing of PVC waste.

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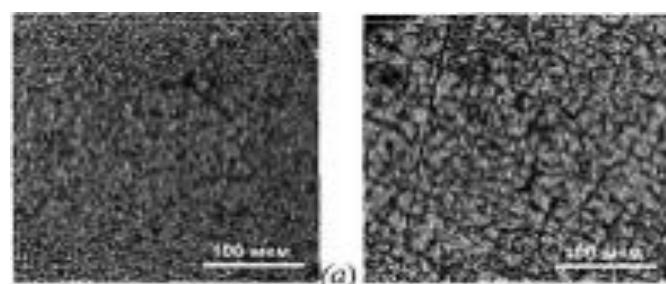
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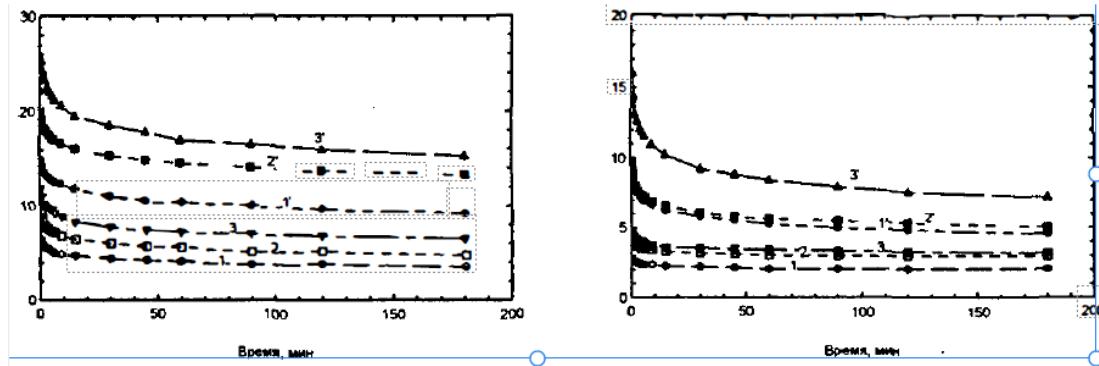
Every year, the areas of application of polymeric materials (PM) are expanding and the requirements for the conditions of their processing and operation are becoming more complicated. The task of extending the service life of a product made of PM is very relevant, since PM is subjected to various influences during processing and operation, leading to a deterioration in their properties and, ultimately, to destruction. In the composition of PM, in addition to the high-molecular polymer, modifying additives are necessarily introduced, without which the processing of PM and the operation of products from them is impossible. At home, it is extremely dangerous to process PVX with heating. Therefore, it is better to look for new uses for plastic products or, if possible, to hand over this plastic for processing, but in Russia it is very difficult for individuals to find collection points for it. Although this is not such

a problem for enterprises, since many PVX producers buy its waste in bulk. The issue of recycling PVX waste after the end of its life is becoming more exciting and relevant, because every year the amount of PVX waste is growing. Quite a few plastic wastes are currently recycled in many developing countries. Over the past few years, European countries and the United States have faced the challenge of recycling so much plastic waste because most of the waste has either been landfilled or incinerated with other municipal solid waste[1]. In this case, graft copolymers are formed, which differ significantly in properties from the corresponding homopolymers and their mechanical mixtures. However, in a number of cases, the glass transition temperature and thermal stability of the obtained copolymers change not so significantly, and sometimes even lead to a decrease in these characteristics. Obtaining three-dimensional cross-linked structures by radical polymerization with the participation of difunctional monomers makes it possible to achieve a significant improvement in the thermal and mechanical properties of polymer systems. In connection with the foregoing, the development of new approaches to the creation of previously unknown heat-resistant high-strength three-dimensional structures with desired properties and easy to process is one of the most important aspects of modern science. At the first stage, oligoamides and oligoimides with terminal amino groups were obtained, which were then treated with a twofold molar excess of acrylic or methacrylic acid chloride in aprotic dipolar amide solvents. The yield of reaction products in terms of the starting monomers was more than 90%[2]. Among man-made wastes, polyvinyl chloride (PVX) makes up 60% of the total amount of polymeric wastes. Recycling waste PVX compared to polyolefins is a bit difficult, so the products made from them have a complex chemical composition, that is, various additives will be added. Given these problems, it is possible to obtain various types of secondary products, modifying them by adding special components that facilitate the processing of PVX waste. These components include virgin PVX, plasticizer, stabilizer and much more. The physical, mechanical and technological properties of the material change significantly during the processing of polyethylene (PE) and polypropylene (PP) waste. During recycling, the polymer is additionally subjected to such influences as mechanochemical and thermal oxidation, and the change in its properties depends on the amount of its processing (multiplicity). As mentioned above, the change in polymer properties in PVX, PE and PP waste recycling processes is related to the amount of materials recycled and scientific research in this field shows that polymer recycling 3-5 times leads to very little change (much less than virgin raw materials) [3]. To compare the molecular weight of primary and secondary PP, measurements of the melt flow index (MFI) were carried out. The measurements were carried out on an IIRT-70M device. Test conditions: temperature 190°C, exposure 5 min, weight 6 g, load 2.16 kg, rod diameter 10 mm, capillary diameter 2 mm. The value of the MFI is calculated by the formula: $g \times 600/t$, where g is the weight of the segment in r , t is the measurement time of the segment (sec). As a result of the measurement, it turned out that the MFI for primary PP is 1.27 g/10 min, and for secondary PP it is 5.35 g/10 min. Thus, the molecular weight of the secondary PP is significantly lower than that of the primary one, which facilitates its crystallization process.

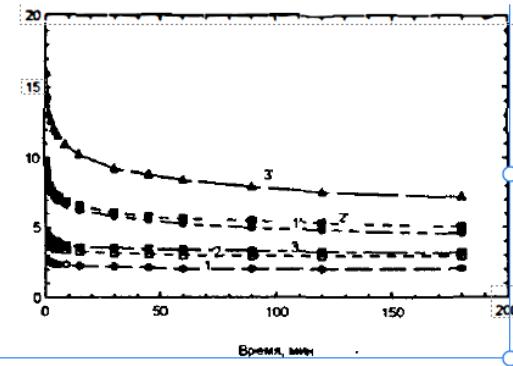


Rice. Fig. 1. Micrographs of the structures of (a) primary and (b) secondary PP.

In the case of LDPE, a somewhat different picture is observed. Figure 20 shows micrographs of films and sections from samples of primary (initial) and secondary LDPE. Since the sizes of the structural elements are almost the same, it was necessary to estimate the degree of crystallinity of the samples. The determination was carried out on a Bruker Smart 1000 diffractometer (λ , [CuKa]=0.71073 Å) at an exposure time of 300 s and room temperature. Sample size 0.5x0.5x0.1 mm. Preliminary experiments have shown that measurements in the range of angles $2\theta = 4-15^\circ$ are the most optimal. To calculate the degree of crystallinity, we used the region $2\theta = 7^\circ-12^\circ$, corresponding to the boundaries of the amorphous halo, in which in all cases two diffraction maxima are observed with interplanar distances equal to 4.14 and 3.75 Å. The profile analysis was performed using the Origin 7.0 program, Origin Lab Corporation , One Roundhouse Plaza Northhampton MA 01060, USA, 1999-2002. The shape of the diffraction maxima is approximated by a set of Gaussian functions. As a result, it was found that the degree of crystallinity for primary and secondary LDPE is 56 and 66%, respectively. These data are consistent with density measurements, which showed that it is 0.93 r/cm³ for primary LDPE and 0.96 r/cm³ for secondary LDPE. Analysis of relaxation properties of materials based on primary and secondary polyolefins. The study of relaxation processes consisted in measuring stress relaxation curves at various permanent strains from 2 to 4% (Fig. 2). It can be seen that both the initial and relaxing stresses for the secondary SP are significantly higher than for the primary one at all strains. Since the geometric characteristics of the samples were exactly the same, this indicates that the secondary PP is much more rigid. The stress relaxation curves for different values of relative strain (2, 3 and 4%) for primary and secondary LDPE are shown in Figure 1. At the same strain E_0 , the stress relaxation curves for primary LDPE are lower than those for secondary LDPE. This leads to the fact that the same picture is typical for the relaxing modules E (Fig. 3). Thus, in order to maintain the same deformation under stress relaxation conditions, secondary LDPE requires large stresses. Another feature is that primary LDPE exhibits linear mechanical behavior over the entire range of deformations E_0 studied, while for secondary LDPE non-linear mechanical behavior is already observed at a deformation of $i:0=3\%$. Relaxation parameters of secondary and primary polyolefins are presented in tables 16 and 17 [4].



Rice. Fig. 2. Curves of stress relaxation of primary (1-3) and secondary (1-3) PP. Deformations are equal: 1, 1-2%, 2.2-3%, 3.3-4%.



Rice. Fig. 3. Stress relaxation curves of primary (1-3) and secondary (-3) LDPE. Deformations are: -2%, 2.2-3%, 3.3-4%.

The processability of PVX is evaluated by the Fikentscher constant, and also, in some cases, by the MFR and the conditions of the manufacturing enterprise [10]. However, the Fikentscher constant does not correlate well with molecular weight due to the large differences in molecular structure and purity of commercial batches of polymer produced by different manufacturers. In addition, the methods for

determining the constant, adopted in the standards of different countries and individual firms, differ. The German DIN standards measure the viscosity of a PVX solution in cyclohexanone at a concentration of 1.0 g/100 ml; JCJ (England) uses dichloroethane at a concentration of 0.5 g/100 ml. The ASTM standard (USA) provides for the measurement of the relative viscosity of a solution at a concentration of 0.2 g/100 ml in cyclohexanone or the measurement of specific viscosity using nitrobenzene at a concentration of 0.4 g/100 ml. The constant was determined according to GOST 14040-82 "Polyvinyl chloride and vinyl chloride copolymers. Method for determining the viscosity number of dilute solutions and the value of K". The results of the experiment are given in table. 1.

Table 1. Determining the flow time of the solution

substance	expiration time, and				
	1	2	3	4	medium
cyclohexanone	3,8	3,7	3,7	3,7	3,7
solution of cyclohexanone and PVC	5,3	5,4	5,4	5,4	5,4

The relative viscosity is:

$$\eta = \frac{t}{t_0} = \frac{5,4}{3,7} = 1,46$$

r/100 cm³

The viscosity number and constant K were determined depending on the relative viscosity (Table 2). From the value of the constant and the viscosity number it follows that the tested PVC can be processed by the extrusion method [4].

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